

PROGRESS REPORT IV

(December 1983 - February 1984)

De-icing and Prevention of Ice Formation of/on  
Offshore Oil-Drilling Platforms

Grantor: U.S. Army Corps of Engineers, CRREL

Hanover, New Hampshire 03755

Grantee: Clarkson University

Potsdam, New York 13676

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4/13/84

TABLE 1

Adhesive Strength and Tensile Modulus of  
LR5630/#500/Silicone Oil (Thomas) Films

Expt. No.	Composition LR-5630/#500/ Silicone Oil	Adhesive Strength kg/cm <sup>2</sup> (-10°C)	Tensile Strength kg/cm <sup>2</sup>		Film Thickness μm
			-10°C	+20°C	
1	100/0/0	0.30 ± 0.18	22 ± 2	10 ± 1	88 ± 8
7	100/10/0	-	27 ± 3	20 ± 3	199 ± 61
3	100/25/0	-	-	16 ± 2	111 ± 11
3'	100/25/0	4.53 ± 3.0	37 ± 4	18 ± 3	61 ± 3
4	100/33/0	-	-	16 ± 2	186 ± 14
2	100/60/0	0.58 (one sample)	69 ± 22	32 ± 13	-
6	100/0/10	0.16 ± 0.05	19 ± 4	8 ± 1	92 ± 8
5	100/25/10	3.78 ± 0.21	29 ± 3	13 ± 1	70 ± 3

± - Standard Deviations

The addition of Tullanox #500 increases the tensile moduli and the adhesive strength (in shear). Addition of silicone oil reduces both quantities.

(2) Next, tensile modulus vs. Tullanox #500 content without silicone oil were measured as a function of temperature. (The values for 100/60 were taken from Table 1, Expt. 2 at +20°C and -10°C.)

TABLE 2

Tensile Modulus as Function of LR5630/#500 Composition  
(No Silicone Oil) and Temperature

Composition	LR5630/#500 →	100/0	100/25	100/33	100/50	100/60
Ball-milling duration for Obtaining Homogeneous Product, h	Temperature °C	-	3	4	5	11
Tensile Modulus kg/cm <sup>2</sup>	20	10 ± 1	32 ± 3	27 ± 9	-	32 ± 13
	10	14 ± 1	34 ± 3	28 ± 11	38 ± 10	54 ± 20
	0	20 ± 4	61 ± 22	49 ± 20	70 ± 13	61 ± 18
	-10	24 ± 3	55 ± 11	57 ± 25	57 ± 11	69 ± 22
	-20	31 ± 4	-	85 ± 30	-	89 ± 16

The tensile modulus increases with increasing Tullanox #500 content of LR5630, e.g. the tensile modulus of the 100/25 film with #500 is about 3 times larger than that of the film without Tullanox #500. Tensile modulus and  $E_{Arrh}$ , the Arrhenius energy of activation, are plotted vs. #500 content in Figs. 1 and 3, respectively. Fig. 2 shows plots of  $\log_{10}$  (tensile modulus in kg/cm<sup>2</sup>) vs.  $10^3/T$ . The tensile moduli for LR5630 plus #500 as a function of film composition (Fig. 1) give higher values than those without Tullanox. Fig. 3 shows that  $E_{Arrh}$  passes through a maximum for LR5630 plus 33% Tullanox 500 (see also Fig. 2). The reason for this is not clear but may be due to defects in the films caused by increasing amounts of the Tullanox powder.

(3) Lexan (polycarbonate)/LR5630/Silicone Oil (Thomas) films. Results for such films were given in Progress Report III (p. 5); additional data are presented here filling in gaps (see Table 3).

TABLE 3  
Adhesive Strength and Tensile Modulus as Function  
of Temperature and Composition for Lexan/LR5630/Silicone Oil (Thomas)  
Films

Composition	Adhesive Strength kg/cm <sup>2</sup> (-10°C)	Tensile Modulus kg/cm <sup>2</sup>		μm
		-10°C	+20°C	
Lexan/LR5630/Silicone Oil (Thomas) 100/50/10	3.05 ± 0.45	789 ± 100	564 ± 90	50
Lexan/LR5630/Silicone Oil (Thomas) 100/10/10	3.00 ± 0.80	688 ± 91	291 ± 42	45

(4) LR5630 and LR3320 plus Silicone Oils-Films.

(a) LR5630/LR3320/Silicone Oil (Thomas).

Further data are added to those in Progress Report III, p. 6.

TABLE 4  
Adhesive Strength and Tensile Modulus of  
LR5630/LR3320/Silicone Oil (Thomas)-Films

Composition LR5630/LR3320/Oil	Adhesive Strength kg/cm <sup>2</sup> -10°C	Tensile Modulus kg/cm <sup>2</sup>	
		-10°C	20°C
100/0/10	0.16 ± 0.05	19 ± 4	8 ± 1
75/95/10	0.09 ± 0.04	32 ± 2	17 ± 2
50/50/10	0.56 ± 0.48	110 ± 11	43 ± 5
27/75/10	4.15 ± 0.12	197 ± 30	93 ± 1.2
0/100/10	2.71 ± 0.64	254 ± 12	138 ± 12

(b) LR5630/LR3320/SF-1154 Silicone Oil-Films.

Here also additional data to those in Progress Report III, p. 7 have been obtained.

TABLE 5

Adhesive Strength and Tensile Modulus of  
LR5630/LR3320/SF-1154 Silicone Oil-Films

Composition  LR5630/LR3320/ Silicone Oil	Adhesive Strength kg/cm <sup>2</sup>  -10°C	Tensile Modulus kg/cm <sup>2</sup>	
		-10°C	+20°C
100/0/20	0.10 ± 0.02	15 ± 2	7 ± 1
75/25/20	0.03 ± 0.01	25 ± 3	9 ± 1
50/50/20	0.71 ± 0.24	39 ± 4	15 ± 1
25/75/20	1.67 ± 0.24	90 ± 7	33 ± 2
0/100/20	0.67 ± 0.12	199 ± 30	80 ± 13

Adhesive strength increases with tensile modulus up to a ratio LR5630/LR3320 = 25/75. But for 0 parts LR5630, the adhesive strength drops considerably (see also Fig. 4). The tensile modulus, however, increases steadily throughout without any sign of the decrease in adhesive strength. Table 6 below completes the second table on p. 7, Progress Report III with tensile modulus data.

TABLE 6

Adhesive Strength and Tensile Modulus For  
LR5630/Thomas Silicone Oil-Film and For LR5630/SF-1154 Silicone Oil  
Film, Respectively

Composition LR5630/Silicone Oil	Adhesive Strength, kg/cm <sup>2</sup> (-10°C)	Tensile Modulus, kg/cm <sup>2</sup>	
		-10°C	+20°C
100/20 Thomas	0.04 ± 0.003	18 ± 5	6 ± 1
100/20 SF 1154	0.10 ± 0.02	15 ± 2	7 ± 1

Thomas silicone oil is only partially miscible with LR5630, but SF-1154 is completely miscible. Nevertheless, the tensile moduli are nearly the same for both cases.

Table 7 completes the last table on p. 7, Progress Report III, giving data for the tensile moduli.

TABLE 7  
Adhesive Strength and Tensile Modulus For  
LR5630/LR3320/Thomas or SF-1154 Oil

Composition	Adhesive Strength kg/cm <sup>2</sup> -10°C	Tensile Modulus kg/cm <sup>2</sup>	
		-10°C	+20°C
LR5630/LR3320/Silicone Oil			
0/100/20 (Thomas)	1.74 ± 0.06	263 ± 25	143 ± 16
0/100/20 (SF-1154)	0.67 ± 0.12	119 ± 30	86 ± 13
25/75/20 (Thomas)	3.43 ± 0.45	198 ± 30	53 ± 5
25/75/20 (SF-1154)	1.61 ± 0.24	90 ± 7	33 ± 2

The tensile moduli are rather large, but the adhesive strengths have only moderately increased.

(c) LR3320/SF-1154-Films

The first table on p. 8, Progress Report III, has now been completed (see Table 8 below).

TABLE 8

Adhesive Strength and Tensile Modulus of  
LR3320/SF-1154 Films

Composition LR3320/SF-1154	Adhesive Strength kg/cm <sup>2</sup> (-10°C)	Tensile Modulus kg/cm <sup>2</sup>	
		-10°C	+20°C
100/0	3.42 ± 0.61	275 ± 70	135 ± 12
100/10	1.21 ± 0.14	177 ± 21	94 ± 9
100/20	0.67 ± 0.12	119 ± 30	86 ± 13
100/50	0.58 ± 0.41	78 ± 9	19 ± 3
100/100	0.31 ± 0.17	36 ± 3	14 ± 1

Below a number of data are being presented of a variety of films.

(d) LR3320/Silicone Oil (Thomas Oil, SF-1154)-Films

TABLE 9

LR3320/Silicone Oil Films

Composition LR3320/Oil	Adhesive Strength, kg/cm <sup>2</sup>		Tensile Modulus, kg/cm <sup>2</sup>			
	Thomas (-10°C)	SF-1154 (-10°C)	Thomas		SF-1154	
			-10°C	+20°C	-10°C	+20°C
100/20	1.74 ± 0.06	0.67 ± 0.12	263 ± 25	143 ± 16	119 ± 30	86 ± 13
100/50	3.62 ± 0.67	0.58 ± 0.41	201 ± 26	107 ± 10	78 ± 9	19 ± 3



(e) LR5630/Silicone Oil-Films

TABLE 10

LR5630/Silicone Oil-Films

Composition LR5630/Silicone Oil	Adhesive Strength $\text{kg/cm}^2$ (-10°C)	Tensile Modulus $\text{kg/cm}^2$	
		-10°C	+20°C
100/0	$0.61 \pm 0.14$	$24 \pm 3$	$10 \pm 1$
100/20 (Thomas)	$0.045 \pm 0.003$	$18 \pm 5$	$6 \pm 1$
100/20 (SF-1154)	$0.10 \pm 0.002$	$15 \pm 2$	$7 \pm 1$

(f) LR5630/LR3322/SF-1154/Thomas-Films

Gaps in the second table of p. 9, Progress Report III, have been filled (see Table 11 below).

TABLE 11

LR5630/LR3320/SF-1154/Thomas-Films

Composition LR5630/LR3320/SF-1154/Thomas	Adhesive Strength $\text{kg/cm}^2$ (-10°C)	Tensile Strength $\text{kg/cm}^2$	
		-10°C	-20°C
100/0/50/10	$0.04 \pm 0.01$	$10 \pm 2$	$4 \pm 1$
100/100/50/11	$0.48 \pm 0.14$	$66 \pm 9$	$20 \pm 2$
100/0/20/14	$0.08 \pm 0.02$	$13 \pm 2$	$6 \pm 1$
100/0/10/10	$0.17 \pm 0.24$	$15 \pm 2$	$8 \pm 1$

(5) Heating of Films Before Testing.

There are indications that the properties of the films become more favorable by moderate heating; this was tested.

The first table on p. 9, Progress Report III, has been completed by tensile modulus data for heated films (the whole table of p. 9, Progress Report III, is repeated here plus the tensile modulus values for the heated films).

TABLE 12

LR5630/LR3320/SF-1154/Thomas-Films  
(Unheated and Heated for 1 h at 105°C)

Composition LR5630/LR3320/SF-1154/ Thomas	Adhesive Strength kg/cm <sup>2</sup> (-10°C)		Tensile Modulus, kg/cm <sup>2</sup>			
			Unheated		Heated	
	Unheated	Heated	-10°C	+20°C	-10°C	+20°C
A { 50/50/20/0 100/0/10/10 25/75/20/0	0.71 ± 0.24	0.12 ± 0.24	39 ± 4	15 ± 1	37 ± 3	17 ± 2
	0.17 ± 0.29	0.04 ± 0.24	15 ± 2	8 ± 1	14 ± 2	7 ± 1
	1.61 ± 0.24	0.75 ± 0.24	90 ± 7	33 ± 2	77 ± 7	36 ± 3
B { 0/100/20/0 25/75/0/10	0.67 ± 0.12	0.67 ± 0.12	199 ± 30	86 ± 13	186 ± 24	67 ± 8
	4.15 ± 0.12	4.05 ± 0.12	257 ± 36	115 ± 9	178 ± 29	93 ± 12

A ~ Heating decreases adhesive strength; B ~ Practically no effect. No systematic change of the tensile modulus is apparent.

The first table on p. 10, Progress Report III has been completed by determining the respective tensile moduli.

TABLE 13

Heating of LR5630/LR3320/SF-1154 = 50/50/20-Films

Heating in Air	Adhesive Strength kg/cm <sup>2</sup> (-10°C)	Tensile Modulus, kg/cm <sup>2</sup>	
		-10°C	+20°C
No Heating	0.71 ± 0.11	39 ± 4	15 ± 1
105°C, 1h	0.12 ± 0.11	48 ± 4	20 ± 4
120-130°C, 1h	0.26 ± 0.11	65 ± 10	25 ± 4
140°C, 1h	0.55 ± 0.11	64 ± 8	20 ± 2

Tensile moduli increased by heating at increasingly higher temperature.

Another film: LR3320/SF-1154 = 100/10 was heated at 90°C for various lengths of time.

TABLE 14

Adhesive Strength in kg/cm<sup>2</sup> (-10°C) LR3320/SF-1154 = 100/10-Film Heated  
at 90°C as Function of Time

	(4 samples)	one sample each			
h	0	1	2.1	4.5	7.5
Adhesive Strength, kg/cm <sup>2</sup>	1.21 ± 0.14	0.82	1.11	1.15	1.24

Heating at 90-105°C for 1 h appears to be beneficial as far as adhesive strength is concerned (compare Tables 12A, 13 and 14).

(6) Shear Adhesive Strength As a Function of Tensile Modulus.

Fig. 5 was obtained by plotting shear adhesive strength data for all samples except those containing Tullanox #500 vs. tensile modulus. Increasing tensile modulus values yield increasing adhesive strength values (linear relation).

(7) Shear Adhesive Strength As Function of Film Thickness.

TABLE 15

Adhesive Strength as Function of Film Thickness

Film (A): LR5630/LR3320/SF-1154 (Silicone Oil) = 75/25/20						
Film Thickness ( $\mu\text{m}$ )	12	42	62	80	98	Av.
Adhesive Strength, $\text{kg/cm}^2$	0.02	0.07	$(0.03 \pm 0.01)^*$	0.06	0.21	$0.092 \pm 0.06$
Film (B): LR5630/LR3320/Thomas Silicone Oil = 75/25/10						
Film Thickness ( $\mu\text{m}$ )	51	58	67	82	100	Av.
Adhesive Strength, $\text{kg/cm}^2$	0.09	0.07	0.12	$(0.09 \pm 0.04)^*$	0.07	$0.09 \pm 0.06$

\* Reported in Tables 4 and 5, respectively.

The effect of film thickness is not large for the above thickness range. The surface of Film A was oily.

### Peeling Strength Apparatus

A peeling strength apparatus has been designed and constructed. Tests are being carried out now to establish whether it is satisfactory. Very small forces are involved, i.e. a few grams/cm<sup>2</sup>. The apparatus and tests will be presented in the next report.

### Stage of Development of the Project at the End of the First Year

A great number of block-co-polymer films of a large variety of compositions have been systematically investigated as to their adhesive strength with respect to ice and their tensile moduli. It is anticipated that the resistance of films to environmental effects (storms, waves) will increase with increasing tensile modulus. Thus, it has been attempted to increase the tensile moduli of the films while increasing their adhesive strength moderately in order to stay within the maximum adhesive strength stipulated for this project, i.e. 25 p.s.i. or 1.76 kg/cm<sup>2</sup>. The data of the most promising films so far are collected in Table 16.

TABLE 16

Most Promising Films Tested Yet

Composition	Adhesive Strength kg/cm <sup>2</sup> (-10°C)	Tensile Modulus, kg/cm <sup>2</sup>	
		-10°C	+20°C
LR5630/LR3320/ Silicone Oil (Thomas)  50/50/10	0.56 ± 0.48	110 ± 11	43 ± 5
LR5630/LR3320/Silicone Oil (SF-1154)  0/100/20	0.67 ± 0.12	199 ± 30	86 ± 13
LR5630/LR3320/Oil  0/100/20 (Thomas)	1.74 ± 0.06	263 ± 25	143 ± 10
LR3320/SF-1154  100/10	1.21 ± 0.14	172 ± 21	94 ± 9
LR5630/LR3320/SF-1154/Thomas  Heated, 105°C, 1h  0/100/20/0	0.67 ± 0.12	186 ± 24	67 ± 8

The best film on the basis of adhesive strength and tensile modulus appears to be:

LR3320/SF-1154 = 100/20

It is, of course, arbitrary to take films which have tensile moduli above  $100 \text{ kg/cm}^3$ ; however, we are designing an erosion test apparatus which will give linear water velocities of up to about 70 m.p.h. This will give a more realistic test for erosion resistance.

In addition, films of still higher tensile modulus and adhesive strength (the latter within the permitted limits) will be prepared. These will consist most likely of chemically crosslinked rubber instead of the block-co-polymers.

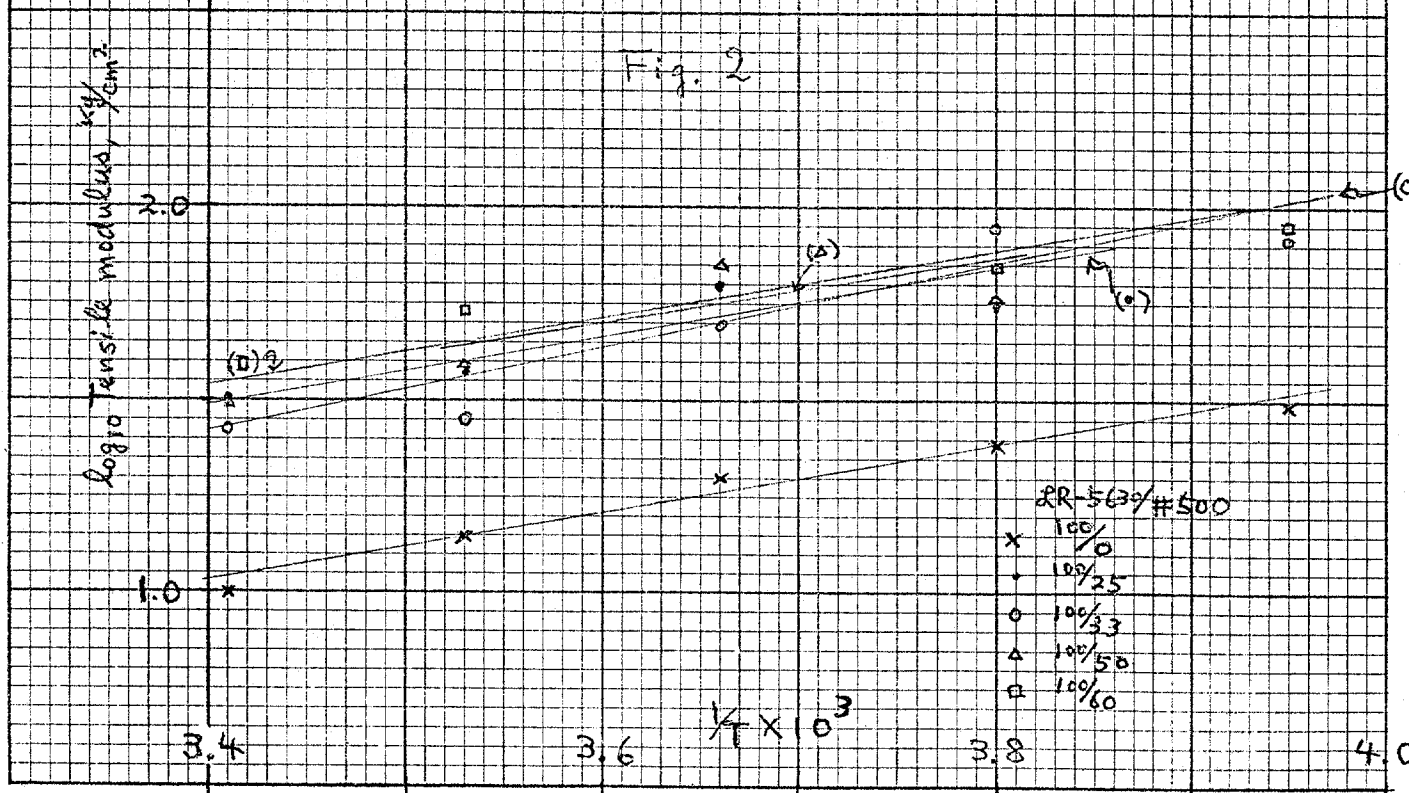
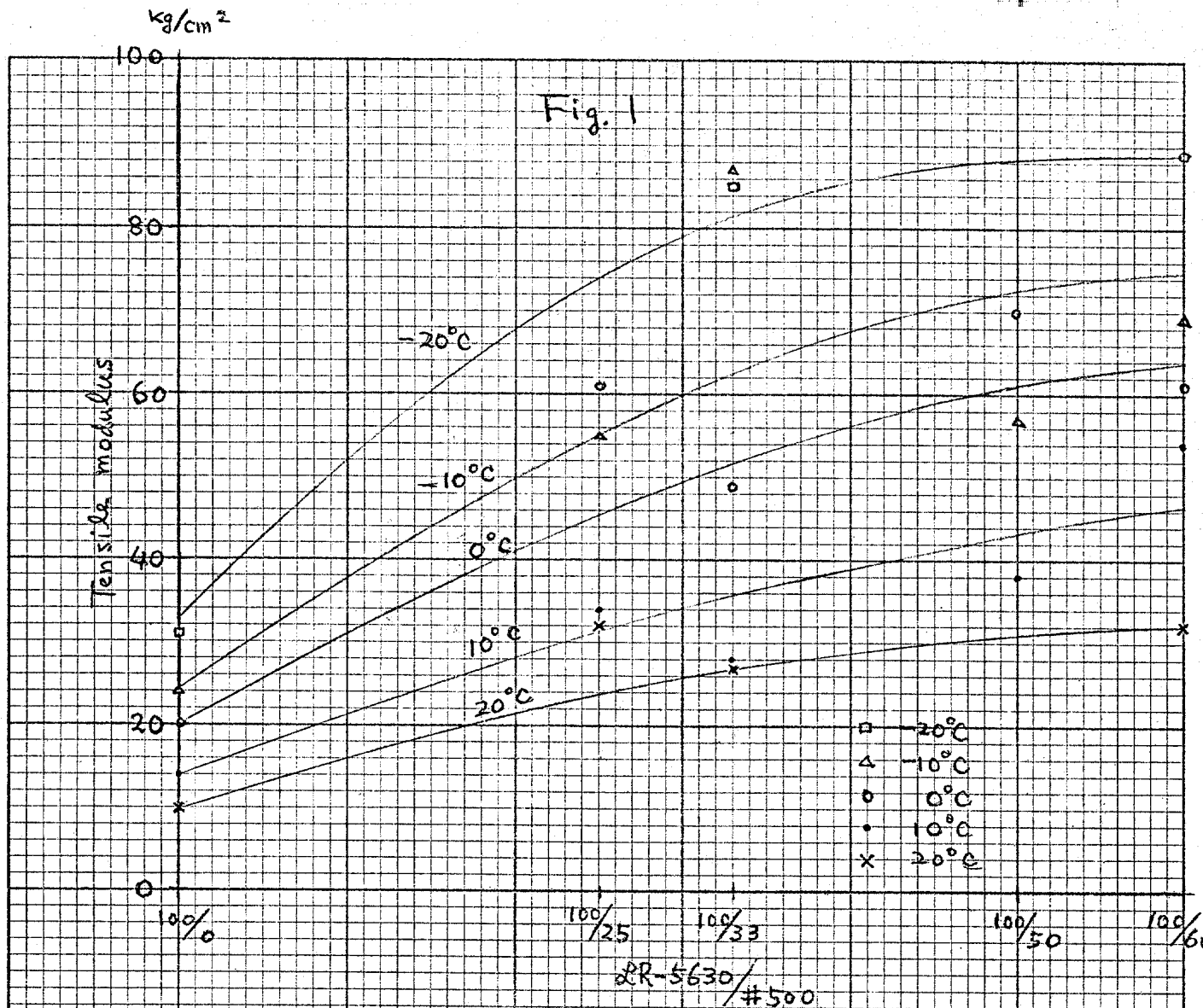




Fig. 3

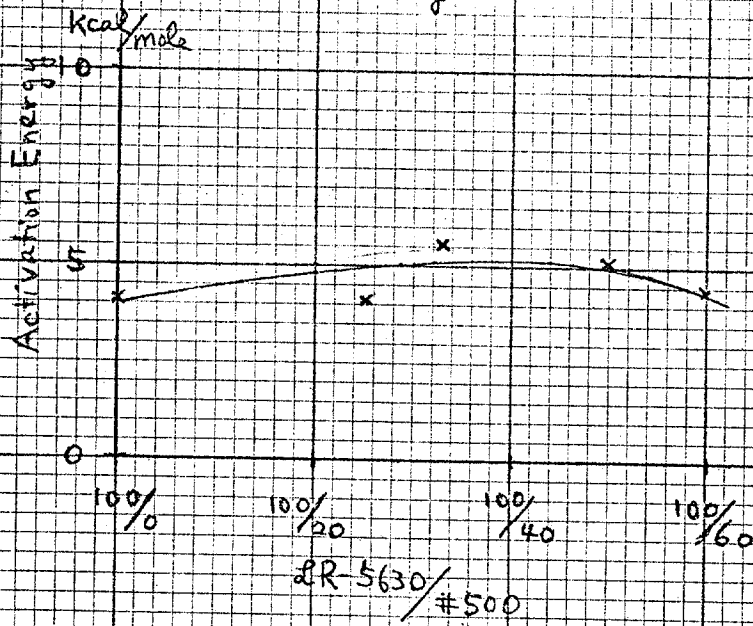


Fig. 4 (TABLE 5)

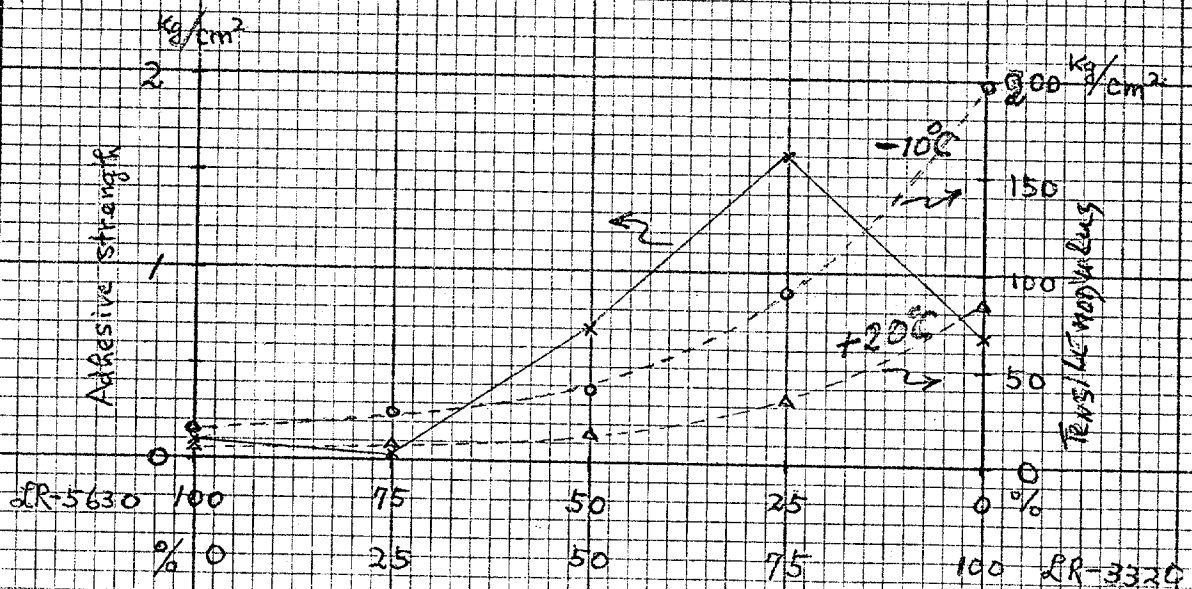


Fig. 5

Adhesive Strength

$\text{kg/cm}^2$

4

3

2

1

0

100

200

300  $\text{kg/cm}^2$

Tensile Modulus at  $-10^\circ\text{C}$

Progress Report V

(March 1 - May 31, 1984)

De-icing and Prevention of Ice-Formation of/on  
Offshore Oil-Drilling Platforms

Grantor: U.S. Army Corps of Engineers, CRREL  
Hanover, New Hampshire 03755

Grantee: Clarkson University  
Potsdam, New York 13676

Grant No.: DACA 89-33-0003

Principal Investigator: Dr. H.H.G. Jellinek  
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DATE SUBMITTED:

6/8/84

Progress Report V

(March 1 - May 31, 1984)

De-icing and Prevention of the Formation of/on

Offshore Oil-Drilling Platforms

by

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The peeling apparatus has been given a more permanent and convenient structure and peeling tests have been continued. In addition, a mixed water-air erosion device has been built which can have speeds of the air/water mixture to 100 m.p.h. or more. A few preliminary tests have been carried out with this instrument.

## I. The Peeling-Strength Tester

This peeling tester has been constructed for very small adhesive forces and is, therefore, first of its kind. Fig. 1 gives schematic drawings of the tester.

(a) view shown from the direction of the arrow which is indicated in Fig. 1(c)

(b) top view

(c) side view

(1) Aluminum cylinder for preparing ice. The film (coating) adheres directly to the ice.

(2) Al-Support for the cylinder.

(3) Part of film peeled off the ice.

(3a) Scotch tape

(4) Statham transducer

(5) Nylon thread ( $\emptyset$  ca. 0.13 mm)

(6) Gear box (reduction ratio 1/50, linear movement of Statham gauge 0.66 cm/min)

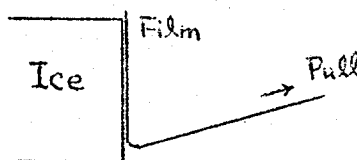
(7) Motor plus another gear box

(8) Graphite sheet (small) for lubrication, resting on an Al-platform with guides.

## (2) Peeling Test Results

The peeling tester is located in the walk-in refrigerator at  $-10^{\circ}\text{C}$ . Electrical leads are passed through a hole in the refrigerator wall to a recorder.

The peeling strength of our co-polymer films was determined which is very small indeed. This results in the special features of the peeling tester. The accompanying drawing illustrates the peeling procedure.



At the moment of measuring the peeling strength, the pull is exactly at a right angle to the ice surface and the film/ice interfacial area (or width) is known. The force required for bending the film depends on the film thickness; as the adhesive strength is so very small it has to be investigated whether the bending strength is negligible. For film thickness see Table 1 below:

TABLE 1

Peeling Tests at -10°C

[The ice/film interfacial area is circular of 2 cm radius; the peeling force is measured when half of the film has been pulled off, i.e. when the width is at its maximum, i.e.  $2R = 4$  cm; the force acts exactly at  $90^\circ$  with respect to the interface (no shear-component).]

(a) LR3320

Film Thickness	Peeling Strength	No. of
<u><math>\mu\text{m}</math></u>	<u><math>\text{g/cm}</math> width (width 4 cm)</u>	<u>Sample</u>
$30 \pm 11$	$15 \pm 9.0$	17
$45 \pm 4$	$20.0 \pm 5.3$	12
54	24.9	2

(b) LR3320 coated with Tullanox #500 Powder

<u><math>\mu\text{m}</math></u>	<u><math>\text{g/cm}</math></u>	<u>No. of Samples</u>
$38 \pm 5$	$4.3 \pm 1.1$	3
$48 \pm 2$	$3.8 \pm 0.6$	4
68	5.2	2

The ratio of the thicknesses in Table (1a) is 1:1.5:1.8 and that of the peeling strengths 1:1.3:1.54. This indicates that the peeling strength is not affected by the film-thickness within experimental error. The

same is nearly the case for Table (1b); thickness 1:1.26:1.79; strength 1:0.9:1.21. However, the peeling strength for Tullanox coated films is about 1/5 of that for the films without Tullanox.

Shear strength measurements gave the opposite results (see Report IV). The adhesive shear-strength is considerably larger for the films with Tullanox than for those without Tullanox 500. This must have something to do with the rougher surface of films having Tullanox powder applied. The Tullanox was spread on the film surface and the excess powder was brushed off. The powdered surface had a milky-white appearance.



(b) Effect of Type of Co-Polymer Film

TABLE 2

Peeling Tests (-10°C)

(1) LR5630

<u>μm</u>	<u>g/cm</u>	<u>No. of Samples</u>
70 ± 16	26.8 ± 5.5	5

LR5630 plus Tullanox #500

<u>μm</u>	<u>g/cm</u>	<u>No. of Samples</u>
65 ± 0.5	4.9 ± 0.5	4

There is no difference in peeling strength between LR5630 and LR3320.

(2) LR3320 Plus Silicone Oil (General Electric SF-1154)

	<u>μm</u>	<u>g/cm</u>	<u>No. of Samples</u>
LR-3320/SF = 100/10 parts	57 ± 3	56.9 ± 14.1	3
LR-3320/SF = 100 plus 500	63	7.1	2

Here the peeling strength appears to be higher than without oil; but a

definite conclusion can only be drawn if more data will be available.

(3) LR-5630/LR-3320/Silicone Oil SF

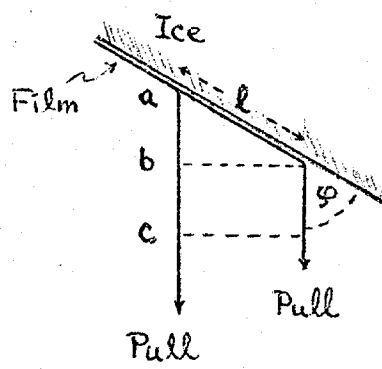
	$\mu\text{m}$	$\text{g/cm}$	<u>No. of Sample</u>
Parts by weight 75/25/10	$95 \pm 3.7$	$28.5 \pm 8.3$	6
Parts by weight 75/25/10			
with #500	$102 \pm 44$	$2.3 \pm 1.4$	3
Parts by weight 25/75/20	$66 \pm 1$	$26.4 \pm 9.3$	3
Parts by weight 25/75/20			
with #500	$90 \pm 20$	$4.0 \pm 0.4$	3

The peeling strength does not appear to be influenced by the composition of the film.

(4) The preparation of the films for measurement proceeded as follows. The cast polymer film is laid on an Al-plate (3" x 3" x 3/16"). An Al-cylinder (inside diameter 4 cm) is placed on film. Boiled out water is cooled and poured into the cylinder. This water is then frozen from the bottom up to the film. It may be noted that the work of peeling is given by

$$W = P (1 - \cos \varphi) \quad (1)$$

$W$  ~ work of adhesion,  $P$  ~ pulling force for 1 cm width of film, length of stripping,  $\varphi$  ~ angle of direction of pulling force with respect to film. This is illustrated in the accompanying sketch.



SEE p. 7.

$\ell$  - length of stripped part of the film.

$\overline{ac} = \ell$ ;  $\overline{bc} = \overline{ac} - \overline{ab} = \ell - \ell \cos \varphi \sim$  descend of load. If  $\varphi = 90^\circ$ , then Eq. (1) becomes

$$W = P \times \ell \quad (1a)$$

This holds for low rates of peeling; our rate is only 6.6 mm/min.

#### (B) Erosion Apparatus; Weathering Tests

An erosion apparatus has been constructed which can produce a water/air stream up to 100 m.p.h. or more. The films adhering to appropriate substrates can be tested for their resistance to such a streams, which simulates gales in nature.

An air-blower supplies air to a glass-tube (30 cm long and of 3.7 cm in diameter). The amount of air is 47.2  $\ell$ /s according to the specifications of the blower. Air coming from an aspirator (connected to a water faucet) delivers 0.27  $\ell$ /s as measured with a flow meter. The amount of water coming from the faucet is via the aspirator into the glass tube was 0.20  $\ell$ /s. This was measured by collecting water for a definite time-interval. Hence, the linear velocity of the exiting water was 99 m.p.h. assuming that the air is carried by the water at its speed.

The distance of the film from the end of the glass-tube was 1.8 cm. It was found that at this distance no back-pressure was generated. A co-polymer film LR5630/LR3320/Silicone Oil (Thomas) 75/25/10 (0.32 mm thick) was exposed to this "gale". The film came off the Al-substrate at some spots after 3 h exposure. Systematic tests will be presented in the

next report. Fig. 2 gives a schematic drawing of the erosion tester.

- (1) Blower (air feed: 47.2 l/s)
- (2) Water-Aspirator
- (3) Wire screen for dispersing water
- (4) Glass tube ("Gale-tunnel"), diameter I.D. 3.7 cm, length 30 cm
- (5) Al-plate substrate coated with a respective adhesion film
- (6) Movable platform
- (7) Flow-meter

#### SUMMARY

- (1) A unique peeling apparatus has been constructed for measuring very weak adhesion. It is the first of its kind.
  - (2) Peeling tests have been performed as a function of the chemical nature of the films and their composition at  $-10^{\circ}\text{C}$ .
  - (3) An erosion tester has been constructed which can simulate gales of 100 m.p.h. or more moving mixtures of dispersed water and air.
- Systematic erosion tests will be presented in the next report.

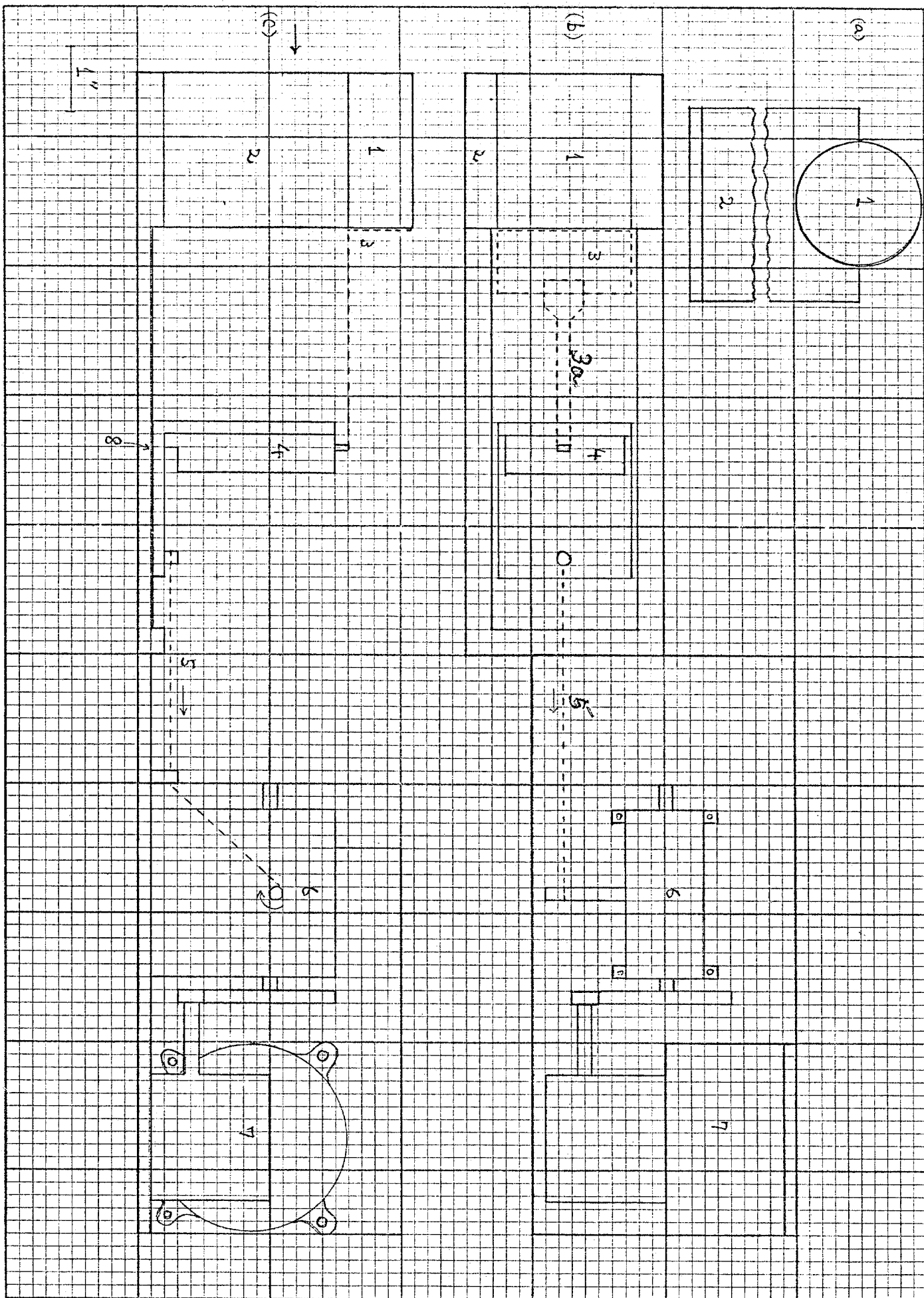
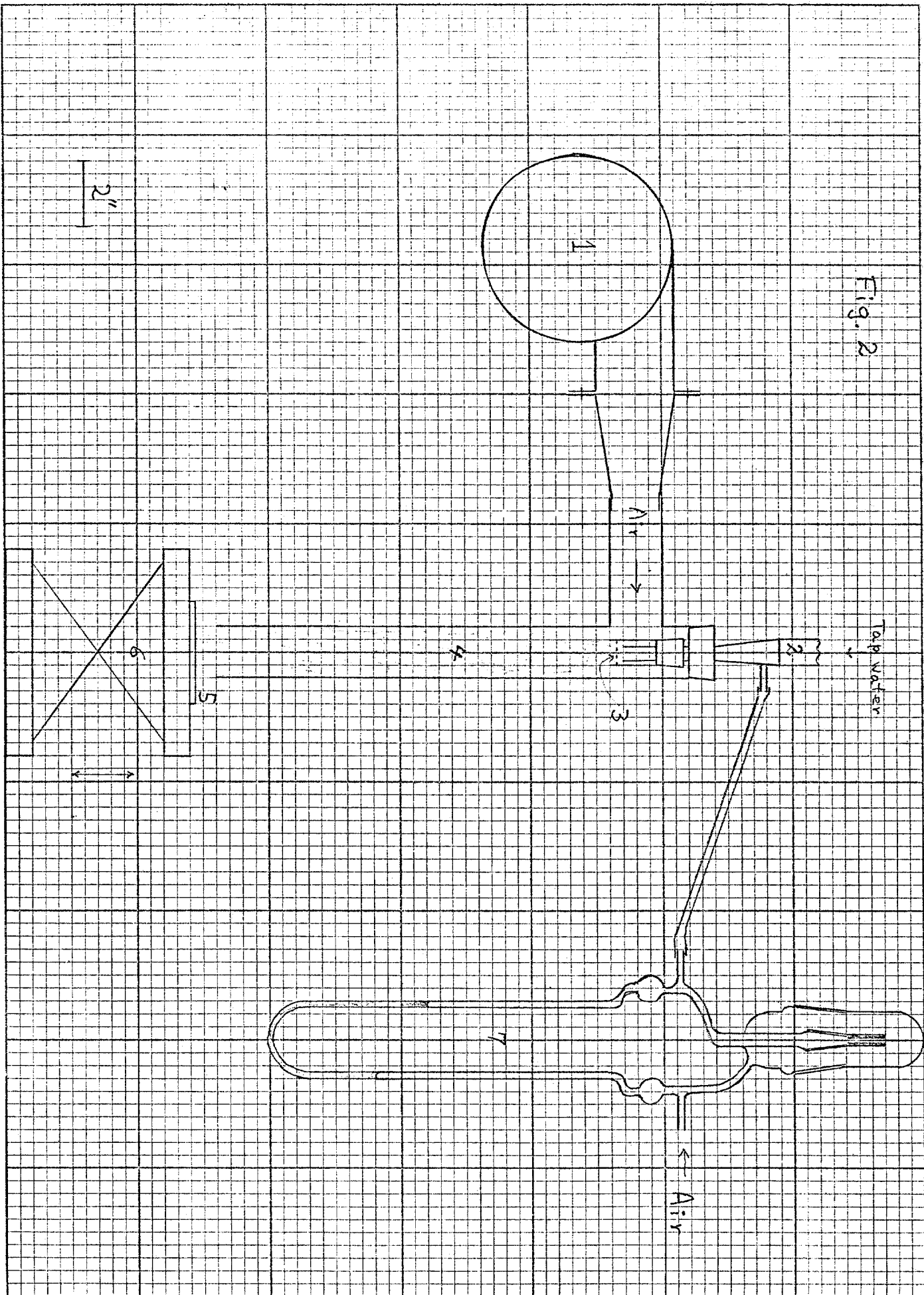


Fig. 2



PROGRESS REPORT VI  
(June - August 1984)

De-icing and Prevention of Ice Formation of/on  
Offshore Oil-Drilling Platforms

Grantor: U.S. Army Corps of Engineers, CRREL  
Hanover, New Hampshire 03755

Grantee: Clarkson University  
Potsdam, New York 13676

Grant No.: DACA 89-33-0003

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DATE SUBMITTED  
10/84



measured (see below). Two adhesive peaks appeared. The first one is due to adhesion (not complete adhesion but only at some patches) between coat/Al and the second to adhesion at coat/ice.

Plate	Coat Thickness mm	Exposure Time h	Shear Adhesive Strength, kg/cm <sup>2</sup>	
			1st Peak	2nd Peak
A	0.20	19.5	0.56	-
B	0.13	0	too weak to measure	
C	0.12	7.0	-	1.78
D	0.22	ca. 3.0	0.74	1.73

The data show that erosion took place; the coats were damaged and they were loosened from the Al-surface; the ice/coat adhesive strength increased as a consequence.

(2) Polycarbonate-polysiloxane Co-polymers XD-11 and 131-848 (see our paper, Colloid and Polymer Sci. 256, 544-551 (1978)) were tested.

These co-polymers have harder coats than that of LR-5630. They also have higher  $T_G$  values than LR-5630.

### Solution for Co-Polymers

XD-11 or 131-848	0.4g	}	dissolved first
$\text{CH}_2\text{Cl}_2$	2.0 ml		
Toluene	2.0 ml		added afterward (131-848 solution is slightly milky)

Al-plates were coated. The XD-11 coat showed small white areas whereas 131-848 was completely white (pencil hardness of either was 4B).

Coat	Shear Adhesive Strength, $\text{kg/cm}^2$	
	Without Erosion	With Erosion (3 h)
XD-11	2.14 (16 $\mu$ )	2.62 (16 $\mu$ )
131-848	2.31 (12 $\mu$ )	2.74 (12 $\mu$ )

In addition to some erosion, the adhesive strength values are too high.

### (3) G.E. Silicone Varnish (Sample 4124)

This varnish is crosslinked on heating yielding a hard coat. Four Al-plates were coated with this varnish and heated at  $100^\circ\text{C}$  for 1 h. Two of the plates were heated subsequently at  $150^\circ\text{C}$ . Two samples were exposed to erosion.

Two other Al-plates were coated with a mixture of Thomas Silicone Oil and Varnish (Oil:Varnish = 2:8). They were heated at  $100^\circ\text{C}$  for 1 h and one

of these plates was exposed to erosion. Results are given below.

Plate No.	Sample (Coat) (Erosion Exposure 3h)	Thickness of Coat $\mu$	Pencil Hardness	Shear Adhesive Strength $\text{kg/cm}^2$
1	varnish 100°, (1 h)	31	3 H	2.50
2	varnish, 100°C (1 h) erosion	35	3 H	1.81
3	varnish 100°C (1 h) → 150°C (1 h)	30	-	2.23
4	varnish 100°C (1 h) → 150°C (1 h), erosion	26	3 H	2.12
5	varnish/oil ~ 100°C	24	-	1.33
6	varnish oil ~ 100°C, erosion	28	4 B	1.77

Samples Nos. 1,2,3,5 were heated at 150°C for one additional hour. Results are presented below (the Nos. are designated by primes).

Shear Adhesive Strength, kg/cm<sup>2</sup>

1'	2.10 (2.50)
2'	2.28 (1.81)
3'	2.36 (2.23)
5'	1.59 (1.33)

Values in parentheses are the adhesive strength values before further heating (see above).

Samples 1',2',3',4',5' and 6' were further coated with Thomas Silicone Oil and designated with double primes.

	Shear Adhesive Strength, kg/cm <sup>2</sup>	Erosion
1"	0.19	None
2"	2.80	After Erosion
3"	0.20	None
4"	1.93	After Erosion
5"	0.35	None
6"	0.20	None

The silicone oil on top of the coat reduces the adhesive strength but was washed off by erosion (jet). The oil is a good softening agent mixed

into the varnish (pencil hardness 6B). Results are given below.

Sample No.	Composition	Preparation	Shear Adhesive Strength kg/cm <sup>2</sup>
7	Silicone varnish/SF1154 =100/10	100°C, 1 h, plus 160°C, 1.5 h	3.76
8	Silicone varnish/SF1154 =100/10	100°C, 1 h, plus erosion 3 h	5.40
9	Silicone varnish/SF1154 =100/20	100°C, 1 h, plus 160°C, 1.5 h	2.98
10	Silicone varnish/SF1154 =100/20	100°C, 1h, plus erosion 3 h	2.01

The relatively large addition of SF1154 silicone oil reduced the shear adhesive strength to ice. However, 10% oil increased the strength after erosion while 20% reduced it only somewhat. Apparently, the oil is washed off. In other experiments, Thomas Oil was mixed with the varnish before coating. Many air bubbles remained in the coat, which was heated at 100° for 1 h before testing. Results were as follows:

Sample	Shear Adhesive Strength, kg/cm <sup>2</sup>
Fresh Coat	0.07
After 3 h Erosion	1.59

Silicone oil was apparently leached out during erosion.

#### (4) Dow Corning Compound 5

This compound is a water-repellent silicone grease. An Al-plate was coated with this compound and exposed to erosion for 30 minutes. However, the compopund was washed off.

(5) LR-5630 Co-polymer Coats

(a) A solution of the following composition was prepared:

LR-5630	2.0 g
Dioxane	4.0 ml
Toluene	4.0 ml

The coat was applied in several stages. The total thickness amounted to 1.20 mm. For the first coating LR-5630 was dissolved in the composition as given above. The next two coatings were carried out with a composition as follows:

LR-5630	2.0 g
Toluene	8 ml

(Apparently, dioxane is not needed at all.)

The results are given below.

Cumulative Exposure Time for Erosion	Shear Adhesive Strength kg/cm <sup>2</sup>
0	0.16
1	0.14
2	0.26
4	0.58
8	1.75

The sample exposed for 8 h to erosion was stored at room temperature (ca.

22°C) to see whether adhesive strength would decrease due to diffusion of the siloxane components to the surface (self-mending). The results were as follows:

Storing Time of Sample After 8 h of Erosion Days	Shear Adhesive Strength kg/cm <sup>2</sup>
12	0.76
16	0.32
19	0.16

It should be noted that the adhesive strength after 8 h exposure is still within the range required by the specifications (i.e., 25 psi or 1.76 kg/cm<sup>2</sup>). However, the mending time is too long. In addition, we want to improve the adhesive strength. Also much longer erosion times will be investigated. Experiments to that effect are in progress.

The coat thickness effect was also investigated. The solution was made as follows:

LR-5630	3.0 g
Toluene	6.0 ml
Dioxane	6.0 ml

The coats on Al-plates were heated at 100°C for 1 h.

The results were as follows:

Exposure	Coat Thickness	Shear Adhesive Strength
h	$\mu$	$\text{kg/cm}^2$
0	60	0.10
1	59	0.84
2	61	0.98
4	39	1.61
8	38	4.48

The thicker the coat the more resistant it is to erosion. This must have something to do with the elastic properties of the coat having sufficient resilience. It should be noted that the sample exposed for 8 hours recovered completely with respect to its adhesive strength within 19 h at room temperature.

A solution of LR-5630 (2 g in 8.0 ml toluene) was coated on an Al-plate, heated at  $100^{\circ}\text{C}$  for 1 h. Next, it was coated with ethoxy-dimethyl silicone  $(\text{C}_2\text{H}_5\text{O})_2\text{Si}(\text{CH}_3)_2$  and stored at room temperature for 16 h. This silicone is expected to be hydrolyzed by water adsorbed from the atmosphere producing a thin silicone oil film. Its thickness was about 0.25 mm and its shear adhesive strength strength  $0.2 \text{ kg/cm}^2$ , however after 1 h erosion the adhesive strength increased to  $4.34 \text{ kg/cm}^2$ .



The effect of coat-thickness of LR-5630 is given below.

Sample No.	Formulation					Heated at 100°C 1 h *	Thick-ness $\mu$	Shear Adhesi- Strength kg/cm <sup>2</sup>
	LR5630 g	CH <sub>2</sub> Cl <sub>2</sub> ml	Toluene ml	Dioxane ml	Methyliso-butyl ketone ml			
1	2.0	4.0	4.0	-	-	+	0.3	0.26
2	2.0	-	4.0	4.0	-	-	0.25	0.04
3	2.0	-	8.0	-	-	-	1.2	0.16
4	2.0	-	7.2	-	8.0	-	0.2	0.34
5	2.0	-	6.0	6.0	-	+	0.06	0.10
6	2.0	-	8.0	-	-	+	0.25	0.12
7	2.0	-	8.0	-	-	+	0.3	0.17
7	2.0	-	8.0	-	-	+	0.6	0.12
7	2.0	-	8.0	-	-	+	0.85	0.12

\* + Heating

- No Heating

No definite relation was found between thickness and strength.

(b) LR-5630/LR-3320 Coats

A solution was made up as follows,

LR-5630	12.0 g	} 75/25
LR-3320	4.0 g	

Toluene	88.0 ml	} 79/31
Dioxane	40.0 ml	

It was coated on Al and heated at 100°C for 1 h; its thickness was 0.1 mm.

Results were obtained as follows:

Cumulative Erosion Time, h	Shear Adhesive Strength, kg/cm <sup>2</sup>
0	0.21
1	0.12
2	4.34

The solution of a mixture of LR-5630/LR-3320 = 75/25 was also coated on Al in different thicknesses. They were again heated at 100°C for 1 h:

Thickness (mm)	Shear Adhesive Strength, kg/cm <sup>2</sup>
0.05	0.54
0.1	0.21
0.6	0.64

The number of samples is too small for proper evaluation, but indications are that there is no relation for thickness in this range of thickness.

(6) LR-3320 Coats

Solutions of this co-polymer were prepared as follows:

LR-3320	1.0 g
Toluene	4.0 ml
Dioxane	4.0 ml

The coat on Al was heated at 100°C for 1 h. The results were as follows (exposed to erosion for several hours) 1.14 kg/cm<sup>2</sup>, prior to erosion 0.20 kg/cm<sup>2</sup>. LR-3320 is harder than LR-5360, but the resistance to erosion was not improved.

The effect of thickness was also investigated. The results were as follows (all coats heated at 100°C for 1 h; no erosion).

Sample No.	Formulation			Thickness mm	Shear Adhesive Strength kg/cm <sup>2</sup>
	LR3320 g	Dioxane ml	Toluene ml		
1	1.0	2.0	6.0	-	-
2	1.0	3.0	5.0	0.1	2.95
3	1.0	4.0	4.0	0.1	0.20
4	1.0	7.0	1.0	0.15	0.49
4	1.0	7.0	1.0	0.35	0.43
4	1.0	7.0	1.0	0.40	0.19

There does not appear to be a relation between strength and coat-thickness in the above range of thickness.

Dioxane is a good solvent for the co-polymers while toluene is much less so. The b.p. and evaporation rates for toluene and <sup>1,4</sup> dioxane are 111°C and 101°C and 4.5 and 5.0 respectively (taking the ethylether evaporation rate as 1). The solubility of toluene in water is 0.047 g/100 g H<sub>2</sub>O, that of dioxane is ∞ at room temperature.

Sample No. 1 contained many tiny gel particles formed during evaporation of solvents. No. 2 had a good appearance.

(B) Coats on Sherwin Williams Hi-Mil-Sher-Tar Epoxy Enamel Coat

Preliminary Experiments

The tar was coated on Al-plates using a roller-coater of 6 mm gap-width. This coat was dried for nine days at room temperature and its thickness (calculated from its weight) was about 0.39 mm. It was difficult to obtain a smooth tar-surface.

This tar was coated with co-polymer solutions as shown below.

Sample No.	Formulation							Thickness (by weight)  μ	Shear Adhesive Strength  kg/cm <sup>2</sup>	
	LR5630  g	LR3320  g	Silicone Oil		Solvents					
			Thomas	SF-1154	p-xylene	toluene	dioxane			
			g	g	ml	ml	ml			
1	2.0	-	0.2	-	20.0	-	-	4	0.61	1.
2	2.0	-	0.2	-	20.0	-	-	4	0.79	1.
3	1.5	0.5	-	0.5	15.0	-	5.0	7	0.37	1.
4	1.5	0.5	-	0.5	15.0	-	5.0	9	0.56	1.
5	1.5	0.5	0.2	-	-	10.0	-	61	0.43	1.

All adhesive strength measurements showed two adhesion peaks. The first (always smaller) one is due to adhesion between the tar/copolymer and the second to the coat/ice interface. The co-polymer coat adheres less well to the tar surface than the ice to the polymer, but the ice/polymer values were appreciably larger than expected. This appears to be due to contamination of the polymer coat by the tar as the latter is soluble to a certain extent in the solvents. Thus, a satisfactory primer has to be applied to the tar surface before a coat of the polymer can be applied. A primer consisting of Butvar B-90 (polyvinylbutyral, Monsanto) was tested (solution: toluene/ethanol 6:4 by volume). This 5% polymer solution was sprayed on the tar surface. This coat was cured (crosslinked) at room temperature for 48 h. However, the shear adhesive strength measurements still showed two peaks, as the results below indicate and the 2nd peak is of similar magnitude as before. The search for a suitable primer will be continued.

Sample No.	Preparation	Shear Adhesive Strength kg/cm <sup>2</sup>	
		1st Peak	2nd Peak
1	1st Butvar coat, 3 $\mu$	0.45	1.51
	2nd Butvar coat, ~3 $\mu$	0.45	1.51
	3rd coat LR5630 + 10% Thomas silicone oil, ca. 12 $\mu$		
2	1st Butvar coat, 3 $\mu$		
	2nd Butvar coat + 15% Thomas silicone oil, ca. 3 $\mu$	1.09	1.67
	3rd coat LR5630 + 10% Thomas silicone oil, ca. 12 $\mu$		
3	1st Butvar coat, 10 $\mu$		
	2nd Butvar coat + 30% Thomas silicone oil, ca. 5 $\mu$	0.65	3.37
	3rd Butvar coat + 30% Thomas silicone oil, 16 $\mu$		

## CONCLUSIONS

The most promising experiments so far are those with thick (at least 1 mm) LR-5630 coats (see A. 5(a)). These appear to have the desired elastic properties (resilience) for withstanding prolonged erosion. The shear adhesive strength values are still in the range required by the specifications (i.e., 25 p.s.i. or  $1.76 \text{ kg/cm}^2$ ) after 8 h exposure to erosion. However, we expect to be able to improve on these values considerably by making the coat still more erosion-resistant and by accelerating its recovery. Such experiments are in progress now. Also the G.E. Silicone Varnish (p.4, etc.) shows some promising features which will be investigated further.

The epoxy-tar surface requires suitable primer; the search for such a compound is also pursued now.